Structure, Stability, Edge States and Aromaticity of Graphene Ribbons

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We determine the stability, the geometry, the electronic and magnetic structure of hydrogen-terminated graphene-nanoribbons edges as a function of the hydrogen content of the environment by means of density functional theory. Antiferromagnetic zigzag ribbons are stable only at extremely-low ultra-vacuum pressures. Under more standard conditions, the most stable structures are the mono- and di-hydrogenated armchair edges and a zigzag edge reconstruction with one di- and two mono-hydrogenated sites. At high hydrogen-concentration "bulk" graphene is not stable and spontaneously breaks to form ribbons, in analogy to the spontaneous breaking of graphene into small-width nanoribbons observed experimentally in solution. The stability and the existence of exotic edge electronic-states and/or magnetism is rationalized in terms of simple concepts from organic chemistry (Clar's rule).

While two-dimensional graphene [1] exhibits fascinating properties such as a relativistic massless-dispersion for its charge carriers and ballistic transport on large distances, its gapless spectrum makes it unsuitable for direct application as a channel in field-effect transistors and other semiconducting devices. This problem might be overcome, and thus open the way to a breakthrough carbon-based electronics, by designing graphene nanoribbons (GNRs) [2] in which the lateral quantum confinement opens an electronic gap, function of the ribbon width. Recent works [3, 4] have shown that the use of lithographic patterning of graphene samples can yield GNRs. However, the reported ribbons have large widths, between 15 and 100 nm, small electronic gap, up to 200 meV, and are characterized by a significant egde-roughness. For practical applications, larger gaps, and correspondingly narrower and smoother-edged GNRs (width $w \lesssim 10$ nm), are desirable. An alternative experimental route [5, 6], that makes use of chemical methods such as solution-dispersion and sonication, has shown that graphene sheets spontaneously break into ribbons of narrow width and smooth edges. Ideally, a combination of the two methods could lead to the design of GNRs having edges of controlled orientation, spatial localization, and electronic properties.

In this regard, the knowledge of the structural and energetic properties of the possible edges, as well as of their thermodynamic stability, is crucial to achieve the experimental control necessary for technological applications [6]. A huge number of theoretical works has recently appeared in the literature on GNRs [7, 8, 9, 10, 11, 12, 13, 14]. In those studies, ribbons are usually chosen with the two fundamental edge geometries, zigzag and armchair, and dangling bonds are saturated with a single hydrogen per carbon atom. Zigzag GNRs have caused a great resonance in the scientific community, due to their surprising electronic and magnetic properties. In fact, zigzag GNRs feature magnetism due to spin-polarized electronic states localized on the edge [7, 8] and they possibly turn to half-metal under high external electric fields [9, 10]. All this has fired the hope to use GNRs in future spintronic-devices [9, 11], even if the robustness of the spin polarization in presence of defects has been questioned [14]. Surprisingly, no attempt has been made so far to study the energetics and thermodynamics of ribbon edges having different hydrogen terminations, as a function of the chemical potential typical of the experimental conditions.

In this work we report density functional theory (DFT) calculations of the energetics and structure of various hydrogen-terminated graphene-nanoribbons edges as a function of the hydrogen content of the environment. We show that magnetic nanoribbons are stable only at extremely low hydrogen-concentrations, challenging to obtain experimentally. They are very reactive and thus unlikely to be stable at ambient conditions. The most stable structures at reasonable hydrogen-concentrations are non-magnetic and have a very low chemical reactivity. They are thus likely to be metastable well beyond their region of thermodynamical stability. We also show that at high hydrogen-concentrations graphene is not stable and spontaneously breaks to form hydrogenated edges. This is analogous to the spontaneous breaking of graphene into small-width nanoribbons observed experimentally in organic compounds solution [5, 6]. Finally, the stability and the existence of exotic electronic edge-states and/or magnetism are fully rationalized in terms of simple concepts from organic chemistry (Clar's rule).

We studied GNRs with different edge-terminations using periodic super-cell geometries with lattice-parameter L (periodicity) along the edge, the two edges having the same configuration. Details of the total-energy calculations are in note [15]. Zigzag edges are denoted as $z_{n_1 n_2 \ldots n_X}$ where n_i stands for the number of hydrogen atoms on a given site, and X is the number of adjacent edge-sites within the periodicity L. Armchair edges
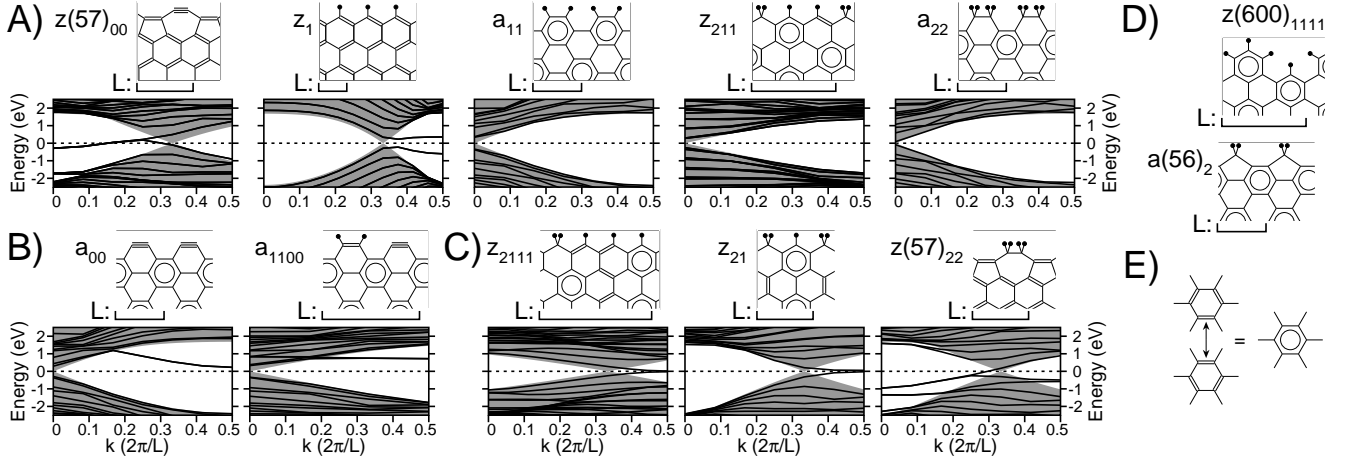
FIG. 1: A: Scheme and electronic band-structure of the five most stable hydrogen-terminated edges of a graphene nanoribbon. Carbon-carbon bonds are represented with the standard notation, while hydrogen atoms are the filled circles. The structures are periodic along the ribbon-edge with periodicity L. The gray area corresponds to the electronic-bands allowed in "bulk" graphene. The dashed line is the Fermi level. B, C: Other stable armchair and zigzag terminations. D: Further examples of possible edges. E: Standard representation of the benzenoid aromatic carbon ring.

are denoted as $a_{m_1 m_2}$ ($a_{m_1 m_2 m_3 m_4}$) for supercells containing one (two) hexagon column(s), where m_i indicates the number of hydrogen atoms bonded to the ith carbon site. Some examples are in Fig. 1. Other structures which do not fit this notation, $z(57)_{ij}$, $z(600)_{ijkl}$, and $a(56)_i$, are also in Fig. 1. Again, the subscripts indicate the number of hydrogens on a given site.

In Tab. I we report the computed zero-temperature edge formation-energy per length:

$$\mathcal{E}_{H_2} = \frac{1}{2L}\left(E^{ribb} - N_C E^{blk} - \frac{N_H}{2}E_{H_2}\right), \quad (1)$$

where E^{ribb}, E^{blk} and E_{H_2} are the total energy of the ribbon super-cell, of one atom in "bulk" graphene and of the isolated H_2 molecule [16]. N_C (N_H) are the number of carbon (hydrogen) atoms in the super-cell. $\mathcal{E}_{H_2}$ can be used to determine the stability of different structures as a function of the experimental conditions [17]. In presence of molecular H_2 gas, at a given chemical potential μ_{H_2}, the relative stability is obtained by comparing $G_{H_2} = \mathcal{E}_{H_2} - \rho_H \mu_{H_2}/2$, where $\rho_H = N_H/(2L)$. At the absolute temperature T and for a partial H_2 pressure P [18],

$$\mu_{H_2} = H^\circ(T) - H^\circ(0) - TS^\circ(T) + k_B T \ln\left(\frac{P}{P^\circ}\right), \quad (2)$$

where H° (S°) is the enthalpy (entropy) at the pressure $P^\circ = 1$ bar obtained from Ref. [19]. In presence of monoatomic-hydrogen gas one should use $G_H = \mathcal{E}_H - \rho_H \mu_H$, where $\mathcal{E}_H = \mathcal{E}_{H_2} - \rho_H \times 2.24$ eV, from DFT.

The most stable structures are thus obtained by comparing G_{H_2} or G_H. G is linear in μ, the slope of the line being determined by ρ_H. For a given value of μ the stable structure is the one with the lowest value of G, thus, by increasing μ (i.e. going to an environment

TABLE I: Formation energy (Eq. 1) and hydrogen density ($\rho_H = N_H/(2L)$) for all the studied edges.

	$\rho_H(\text{Å}^{-1})$	$\mathcal{E}_{H_2}(\text{eV/Å})$		$\rho_H(\text{Å}^{-1})$	$\mathcal{E}_{H_2}(\text{eV/Å})$
$z(57)_{00}$ †	0.000	0.9650	$a(56)_0$ *	0.000	1.4723
z_0 *	0.000	1.1452	a_{00} ∘	0.000	1.0078
z_{100} *	0.136	0.7854	$a(56)_1$ †	0.235	0.7030
z_{200} *	0.271	0.7260	a_{1100} ∘	0.235	0.4946
z_{110} *	0.271	0.4306	a_{10} *	0.235	0.6273
$z(57)_{11}$ †	0.407	0.3337	a_{11} ∘	0.469	0.0321
z_1 *	0.407	0.0809	$a(56)_2$ ∘	0.469	0.4114
z_{211111} *	0.474	0.0463	a_{21} *	0.704	0.2092
z_{21111} *	0.488	0.0397	a_{2211} ∘	0.704	−0.0163
z_{2111} †	0.508	0.0257	a_{22} ∘	0.939	−0.0710
z_{211} ∘	0.542	0.0119			
$z(600)_{1111}$ ∘	0.542	0.0459			
z_{21} †	0.610	0.0382			
z_{221} *	0.678	0.1007			
z_2 *	0.813	0.2224			
$z(57)_{22}$ †	0.813	0.2171			

† Non magnetic,   metallic edges, non aromatic
∗   Magnetic,   metallic edges, non aromatic
∘ Non magnetic, non-metallic edges,   aromatic

richer in hydrogen) the favorable structures will be those with higher hydrogen-density ρ_H. This concept is visualized, as usual [17], by plotting G vs. μ in Fig. 2, where we report the five most stable structures. In Fig. 3, we report the same plot for the most stable edges in the two distinct families of zigzag and armchair GNRs.

Some important conclusions can be driven from Fig. 2. First, the magnetic z_1 edge, widely studied as a potential component for future spintronic devices [9, 11], and the $z(57)_{00}$, proposed in [13], are stable only at extremely low hydrogen-concentrations. Second, at reasonable hydrogen pressure (at ambient conditions, the partial H_2 pres-
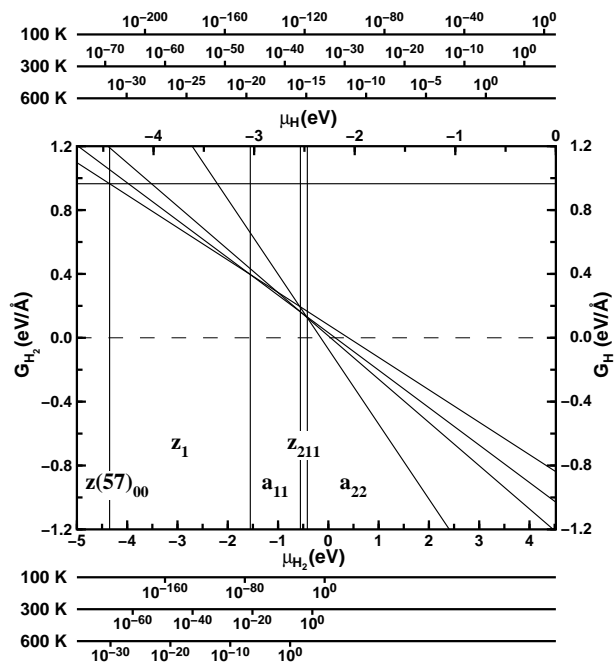
FIG. 2: Formation energies versus chemical potential for the five most stable edges. Vertical lines distinguish the stability regions. The alternative bottom (top) axes show the pressure, in bar, of molecular H_2 (atomic H) gas corresponding to the chemical potentials at T = 100, 300, and 600 K.
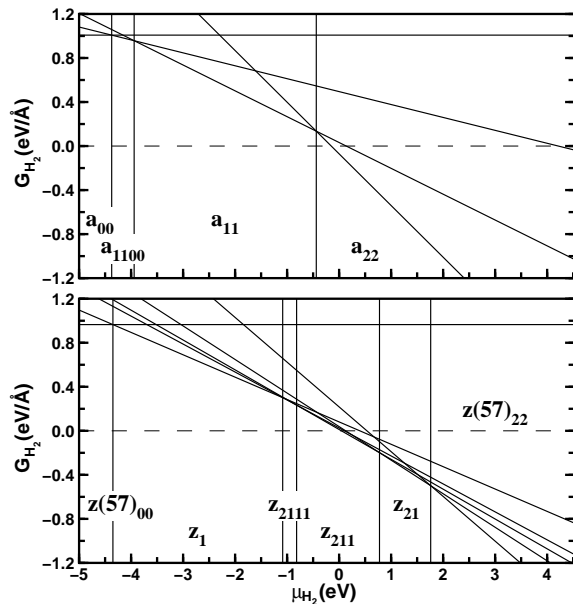

FIG. 3: Formation energies versus chemical potential for the most stable armchair (top) and zigzag (bottom) edges.

sure in air is $\sim 5 \times 10^{-7}$ bar) the most stable edges are a_{11}, z_{211}, and a_{22}. Finally, Fig. 2 shows that graphene is not stable at high hydrogen-concentration (G becomes negative) and spontaneously breaks to form hydrogenated edges. Similarly, it has been experimentally observed

that small-width nanoribbons spontaneously form in organic compounds solutions [5, 6].

We indicate in Tab. I, along with the energetics, whether the proposed edges are magnetic or not, *i.e.* whether a finite magnetization density is observed within DFT calculations. In Fig. 2, we also report the electronic bands of the ribbons and we show the bands of two-dimensional "bulk" graphene projected on the one-dimensional Brillouin zone of the edge (gray area in Fig. 2). As currently done in surface physics, we call "edge states" (ESs) those electronic states localized at edges, having an energy which is not allowed in the bulk (*i.e.* those bands which are outside the gray area in Fig. 2). Such states are localized near the edge. Moreover, in Tab. I we indicate as "metallic edges", those having partially-filled ESs, *i.e.* having ESs which, in absence of magnetic order, cross the Fermi level, and are thus only partially occupied. For a system with partially filled ESs, in a ribbon, it might be energetically convenient to split those bands by inducing a magnetic order between the two ribbon-edges and thus opening an energy gap, as in the well-known case of the z_1 edge. Finally, we remind that the chemical reactivity of a given system can be quantitatively expressed as proportional to the electronic density of states near the Fermi level. As a consequence, all the structures having edge-states crossing the Fermi energy or in its immediate vicinity (independently on whether they are magnetic or not) are expected to be extremely reactive, since the edge-states are available to form chemical bonds.

With these concepts in mind, we remark that the most stable structures at standard and high hydrogen-concentrations, namely a_{11}, z_{211}, and a_{22}, have no edge states, in agreement with the experimental observation of large semiconducting gaps in narrow ribbons [6]. This implies that, besides being non-magnetic, they have a very low chemical reactivity. As a consequence, once formed, those edges are likely to be metastable well beyond their respective windows of thermodynamical stability in Fig. 2. On the other hand, magnetic edges, as the well studied z_1, are stable only at extremely low hydrogen-concentrations and are also very reactive and thus unlikely to be stable at ambient conditions.

We now show that the electronic structure of the edges can be interpreted in terms of aromaticity and according to Clar's rule, well known in organic chemistry since the 60's [20, 21]. The fundamental stability-criterion for hydrocarbons is that each carbon atom must have four saturated bonds. In organic chemistry, the so-called benzenoid aromatic ring can be defined as a resonance (due to the delocalization of π electrons over the ring [22, 23]) between 2 hexagonal rings with alternating single and double bonds as in Fig. 2-E. For such a structure, all the bonds sticking out of the hexagon are single bonds and, as a consequence, two benzenoid rings cannot be adjacent. The energetic stability of a structure increases

with the number of possible resonances. As a consequence, since a structure containing n benzenoid rings displays 2^n possible resonances, the most stable isomer of a given hydrocarbon is the one that maximizes the number of benzenoid rings (Clar's rule [20, 21]). Bulk graphene is the ideal case of aromaticity since there are three equivalent representations in which all the π electrons belong to a benzenoid ring and no double-bonds are present. In such a representation 1/3 of the graphene carbon-hexagons are benzenoid rings.

The edge structures of Fig. 1 are displayed in a representation that maximizes the number of benzenoid rings. However, the resulting ring-density for some of the structures (e.g. the z_{21} or z_{2111}) is lower than the ideal graphene 1/3 density. We analyzed all the edges of Tab. I and we indicate as "aromatic" those structures that have a density of benzenoid rings of 1/3 (e.g. the a_{11}, z_{211} and a_{22}). We note that *all the aromatic structures do not have partially-filled edge-states (are non-metallic) and viceversa.* This empirical rule is valid for all the structures presently studied and can be understood in terms of the Clar's rule. In fact, whenever the ring-density near the edge is smaller than 1/3, there is a competition between the bulk, where aromaticity prevails with an exponential (2^n) weight, and the edge. It is precisely this competition that, imposing the ring density of the bulk, forces some edge carbon-atoms to have less or more than 4 saturated bonds and, thus, originates the electronic "defects", *i.e.* the edge states. The z_{211} and the $z(600)_{1111}$ ribbons are the only zigzag edges compatible with the aromaticity of the bulk. These edge configurations have in fact the same 1/3 periodicity along the zigzag edge as the benzenoid rings of "bulk" graphene. Moreover, mono- and di-hydrogenated armchair edges are both compatible with the 1/3 aromaticity of graphene, whereas asymmetrically passivated edges, such as a_{21}, are not. Notice that, *for a given H density, the most stable edges are aromatic, if an aromatic structure is compatible with such a concentration.* The stability of fully-aromatic edges is confirmed by the fact that polycyclic aromatic hydrocarbons whose structure can be fully represented by benzenoid rings (without double bonds) show particularly high stability, high melting points, low reactivity [22], and have, whenever possible, a_{11} or $z(600)_{1111}$ edges [23, 24].

Concluding, the knowledge of the structure and stability of the possible edges is a crucial issue to control the experimental conditions of the formation of graphene nanoribbons of desired properties. Here, we determined the structure and stability of hydrogen-terminated nanoribbons. For reasonable hydrogen concentrations the most stable structures are the a_{11}, a_{22} and z_{211}, which are not magnetic and do not present valence electronic states localized at the edge. These structures are, thus, expected to be non-reactive and metastable well beyond the region of their thermodynamic stability. In particular, at high hydrogen concentrations graphene spontaneously breaks into a_{22} nanoribbons. Our results are rationalized by means of simple concepts of organic chemistry that can be used to guide the search for the most stable edges in different chemical environments.

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[15] *Ab-initio* calculations are done with the PWSCF code (S. Baroni *et al.*, www.quantum-espresso.org) within plane-wave/ultrasoft-pseudopotential approach and exchange-correlation from Ref. [25]. We used a kinetic energy/charge cut-off of 30/300 Ry. Edges are simulated within a super-cell geometry using a vacuum layer of 9.5 Å between two edges and of 8.5Å between two graphene planes. L is fixed according to the lattice-constant of graphene (2.46 Å) and atomic positions are allowed to fully relax. For armchair edges, the width of the ribbons vary from 21.5 Å for $a(56)_0$ to 24.1 Å for a_{11}. For zigzag, the widths vary from 28.81 Å for $z(57)_{00}$ to 30.72 Å for z_1. Electronic integrations are done using grids (along the periodic direction of the ribbon) of 12 k-points for armchair ribbons and 24, 12, 8, 6, 4, 4 k-points for the zigzag ones with 1, 2, 3, 4, 5, 6 periodicity.
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